

Extended Abstract for “The Role of High Mountains in the Global Transport of POPs”:  
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## **Semi-Volatile Organic Compounds in Snow from National Parks of the Western United States**

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### **INTRODUCTION**

There is reason to believe that the high mountains of western North America, including the Rockies, Cascades, Olympics, and Sierras Nevadas, play a key role in the global transport of persistent organic pollutants (POPs) and other semi-volatile compounds (SOCs). These high mountains, whose highest peaks extend to an elevation of 4300 m in California and 6100 in Alaska, intercept air masses traversing the Pacific Ocean from Eurasia. While data is limited, results from several studies indicate that meteorological events in Eurasia entrain pollutants in westerly winds headed towards North America (1). As industrialization expands in Pacific Rim countries, episodic releases of pollutants are expected to increase. Because airborne contaminants are known to undergo deposition at relatively cold temperatures, such as those found in high mountains, it is likely that the mountains of western North America are accumulating contaminants originating both in North America and in distant locations.

SOCs are preferentially removed from the atmosphere in cold environments due to the reduction in vapor pressure that they experience with decreasing temperature (2). Decreasing temperatures thereby enhance the partitioning of SOCs to particle and ice surfaces in the atmosphere. Snowfall is a significant route of atmospheric deposition because (a) snow is efficient at scavenging both particle-bound and vapor-phase SOCs (3) and (b) snow is the dominant form of precipitation in high mountains; in North American high mountains, snow accounts for 50 to 90 percent of the annual precipitation. SOCs have been detected in snow located in the Canadian Rockies (4), the Yukon (5), and the Sierra Nevada Mountains (6). However, there is a general lack of information concerning the nature, magnitude, spatial distribution, and sources of SOCs in western North America. The U.S. National Park Service is concerned about the suspected but unverified role that high mountains in North America play in the global transport of SOCs due to the prevalence of high-elevation ecosystems under its jurisdiction. In

response to this concern, it initiated a 5-year project entitled the “Western Airborne Contaminants Assessment Project (WACAP)” in 2002 (7).

WACAP aims to address a number of questions regarding the presence, spatial distribution, ecological impacts, and sources of SOCs in National Parks of the western U.S. To accomplish the broad goals of WACAP, a number of interconnected ecological components are being sampled. These include snow, lake water, fish, lake sediments, vegetation, and moose meat. Samples are being analyzed for both semi-volatile organics and metals. Sampling campaigns are scheduled for 2003, 2004, and 2005. The work presented herein concerns organic pollutants in snow samples collected in 2003. The WACAP objectives addressed by this portion of the larger project are:

- 1) To determine if current-use and banned SOCs are present in snow collected at national parks in the western U.S.
- 2) If present, to determine how SOC concentrations in snow vary between different parks and
- 3) To use this information to help formulate hypotheses regarding SOC source contributions in national parks.

### **APPROACH**

Eight National Parks in the western U.S. were selected for snow sampling by WACAP. These include Sequoia, Rocky Mountain, Olympic, Mt. Rainier, Glacier, Denali, Noatak, and Gates of the Arctic. These parks are located across a latitudinal gradient ranging from 36° N to 68° N, a longitudinal gradient ranging from 105° W to 160° W, and an elevational gradient ranging from 427 m to 3030 m. Parks can also be differentiated in terms of the different types of regional pollution sources they are likely to receive and their likelihood of being impacted by trans-Pacific air masses. Two sites were selected for sampling in each park (except in the cases of Noatak and Gates of the Arctic where one site was selected for each), for a total of 14 field sites. These sites are located in or near the watersheds of WACAP lakes selected for water, sediment, and biological sampling so that SOC movement between ecosystem components can be evaluated.

Snow samples were collected in small clearings or open areas on cooler, north-facing slopes located at least 200 m from potential sources of contamination (e.g. roadways, snowmobile trails, or aircraft landing zones). Sampling was conducted in March and April of 2003, near the time of annual maximum snow accumulation but before the onset of spring melting. Snowpits were excavated to the ground, physical characteristics of the snow were measured, and a vertical column of snow was cut from the pit face. Approximately 50 kg of snow were collected per sample in Teflon bags. Samples were shipped on dry ice and stored at -20 °C until analysis.

The analytical method used in this project was designed to quantify a wide array of SOCs. The target analyte list includes 85 SOCs; it includes SOCs that are currently used in the U.S. (e.g. organophosphorus pesticides and triazine herbicides), SOCs that are currently banned in the U.S. (e.g. organochlorine pesticides and PCBs), pesticide degradation products, and combustion products (PAHs). At the time of analysis, snow

samples were removed from the freezer and allowed to melt without heat. Analytes were extracted from melted snow using a novel solid-phase extraction method that enables a number of analyte classes to be extracted in one step. Large-molecular weight interferences were removed from samples with gel permeation chromatography. Polar interferences were removed from samples with silica gel adsorption chromatography. Analytes were separated, detected, and identified using gas chromatography with mass spectrometry. Depending on the analyte, either electron impact or electron capture negative ionization was employed. Quantification was conducted against stable-isotope labeled surrogates that were injected into the melted snow prior to the extraction step. Detection limits were particularly low due to the use of large samples (50 kg of snow per sample). Lower quantification limits for most compounds ranged from 0.06 to 0.006 ng/L.

## **RESULTS**

SOCs were present in snow collected at high-elevation sites in national parks of the western U.S. Chlorthalonil, chlorpyrifos, dacthal, and endosulfan are examples of detected SOC<sub>s</sub> that are currently used in the U.S. Dieldrin, chlordane, hexachlorobenzene, and polychlorinated biphenyls are examples of detected SOC<sub>s</sub> that are currently banned from use in the U.S. Overall, concentrations of current-use SOC<sub>s</sub> were higher than those of banned SOC<sub>s</sub>. In a number of cases, significantly different concentrations of current-use SOC<sub>s</sub> were observed between parks, indicating that the distribution of SOC<sub>s</sub> between parks is influenced by regional sources. As an example, snow from Sequoia National Park contained 25 times more chlorpyrifos than that from Rocky Mountain National Park and 85 times more than that from Denali National Park. It is not surprising that relatively high concentrations of chlorpyrifos were found in snow from Sequoia National Park since it is used as a dormant insecticidal spray during the late winter months in nearby agricultural-intensive areas. Isomeric ratio analysis also indicated that some sources of current-use SOC<sub>s</sub> varied between parks. Concentrations of banned SOC<sub>s</sub> varied less between parks than did those of current-use SOC<sub>s</sub>, indicating that banned compounds are more equally distributed in the northern hemisphere than current-use SOC<sub>s</sub>. On the other hand, particularly high concentrations of certain banned SOC<sub>s</sub> relative to others may indicate that these SOC<sub>s</sub> are being transported to North America from countries that still use them. Because a number of SOC<sub>s</sub> that are banned in the U.S. are still in use in developing Asian countries, it is possible that they were transported to North America by trans-Pacific transport.

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